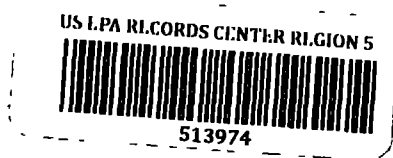


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Quality Assurance Project Plan for the
Measurement of PAH Compounds at ng/L
Levels by Gas Chromatography/Mass Spectrometry

Prepared for CH₂M Hill

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3. PROJECT DESCRIPTION

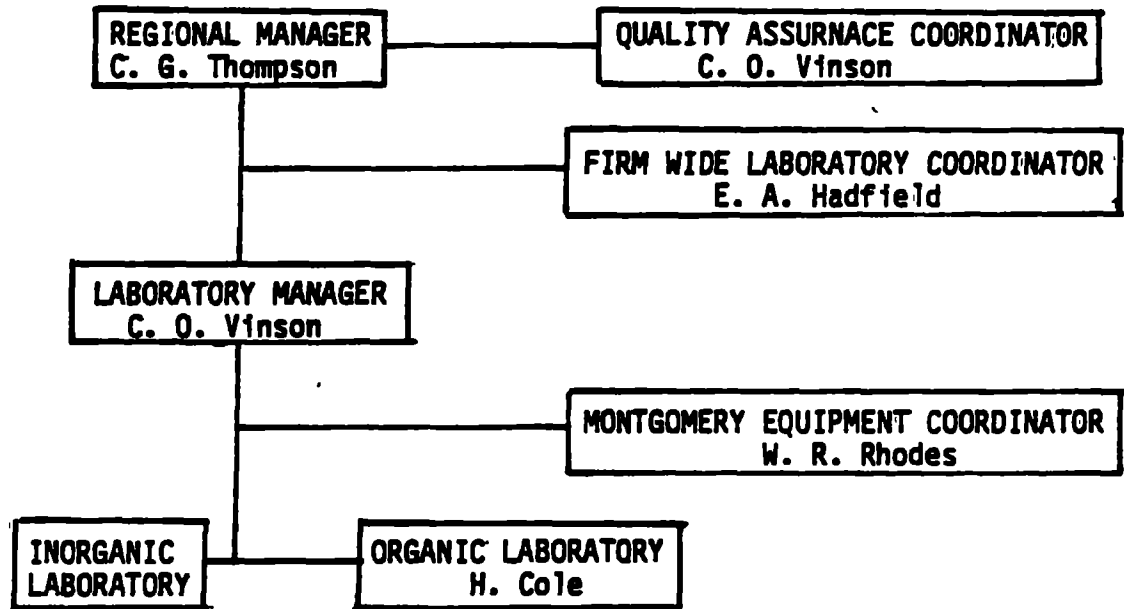
CH₂M Hill is to conduct a project to measure the PAH concentration at ng/L levels in:

- o the ground water in the vicinity of Saint Louis Park, Minnesota,
- o the influent, the effluent, and various stages of the existing treatment facility,
- o various stages during a series of bench scale treatments,
- o the influent and effluent of a pilot plant during a 30 day study.

The analytical procedure involves the serial extraction of the aqueous sample with methylene chloride at pH >11 and then pH <2, concentration, and analysis via capillary column gas chromatography/mass spectrometry (GC/MS).

The anticipated sampling schedule is given in Table 1. The target compounds are listed in Table 2. The PAH measurement data will be used to judge the treatability of the selected treatment process.

4. PROJECT ORGANIZATION AND RESPONSIBILITY



- 4.1 The Regional Manager will review all QA data with the Laboratory Manager on a quarterly basis.
- 4.2 The Laboratory Manager is responsible for the continuity and control of the QA program.
- 4.3 The Quality Assurance Coordinator is responsible for:
 - 4.3.1 Logging samples and introducing control samples.
 - 4.3.2 Monitoring QA activities.
 - 4.3.3 Informing the staff and management of non conformance to the QA program.
 - 4.3.4 Reviews purchased materials to ensure that quality materials are purchased.
 - 4.3.5 Receives data prior to reporting and maintains QA documents.

5. QA OBJECTIVES FOR PAH MEASUREMENT DATA IN TERMS OF PRECISION, ACCURACY, COMPLETENESS AND METHOD DETECTION LIMITS

- 5.1 The QA objective for precision is an average relative range for duplicate analyses of less than 30% at a 95% confidence level. The preliminary validation study indicates that the relative standard deviation of laboratory control standards exhibits a slight concentration dependence (Figure 1).
- 5.2 The QA objective for accuracy is an average bias for the spiked samples of less than 25%. The preliminary validation study exhibited an average bias of -8% and -18% for 15 PAH compounds for true values of 10 ng/L and 25 ng/L, respectively and an average bias of -3% for 27 compounds at a nominal value of 4 ng/L.
- 5.3 The QA objective for completeness is 90%. No more than 10% of the data is to be ruled invalid due to QA/QC checks on the overall system performance.
- 5.4 The QA objective for method detection limit (MDL) is an average MDL of less than 5 ng/L. The validation study gave an average MDL of 1.2 ng/L for the 27 compounds listed in Table 3.

6. SAMPLING PROCEDURE

- 6.1 Method 624, purgeables, requires a duplicate sample to be collected and preserved with acid if analysis is to be performed between 7 and 14 days after collection due to the potential biological degradation of benzene, toluene, and ethylbenzene. If not acid preserved, the purgeable samples must be analyzed within 7 days..
- 6.2 The PNA compounds are susceptible to photodegradation, therefore, amber containers or foil wrapped containers must be used. Extraction must be completed within 7 days of collection. Extracts must be analyzed within 40 days of extraction.
- 6.3 Sample containers must be scrupulously cleaned. All sample containers are to be washed with detergent, rinsed with tap water, reagent water, and set aside to dry. PNA sample containers, after drying, are rinsed with a polar and a non-polar organic solvent and again set aside to dry before use.
- 6.4 Triplicates, duplicates and field blanks are included in each set of samples as scheduled on Table 1. The field blank is sent from the lab to the field and back to the laboratory with the other samples.
- 6.5 The composition of the duplicates and triplicates must be homogenous. Collect these samples in as short a period of time as possible. Fill each bottle of a duplicate or a triplicate set by sequential thirds to ensure homogeneity.
- 6.6 When sampling inactive wells, record the number of well volumes that have been pumped prior to filling an individual sample. A minimum of 10 casing volumes should be pumped before collecting a sample.
- 6.7 When sampling an active well, record the number of gallons pumped in the previous 24 hours.
- 6.8 The specific sample tag is illustrated in Figure 2.
- 6.9 Field records must be completed at the time the samples are collected. The records must be signed or initialed including the date and time by each member of the sampling team. A Field Tracking Report Form is given in Figure 4.

7. SAMPLE CUSTODY

- 7.1 Chain of custody procedures will apply to all samples. A chain of Custody Record form is given in Figure 5. All entries are to be completed in indelible ink. Dean Malotky is the field sampling team leader.
- 7.2 The original chain of custody record is sealed in a watertight plastic sandwich bag and shipped inside the sealed transportation case. A copy of the record is retained by the sampling team.
- 7.3 The samples are shipped to Harold Cole, the designated custodian at CH₂M Hill. A permanent log book will be kept describing the samples as received. Log book entries are to include; the person delivering the sample, date and time received, source of sample, sample ID or log number, mode of transport, and the condition of the sample as received.
- 7.4 Samples are to be stored in the custody room, a securely locked area. Only the custodian is to deliver samples to the laboratory personnel. The laboratory is to be maintained as a secured area, restricted to authorized personnel only. Laboratory personnel are responsible for the care and custody of the sample after being received from the custodian. The sample must always be in the possession or view of the laboratory personnel or secured in the laboratory at all times until analysis is completed.
- 7.5 The unused portion of the sample, if any, and all identifying labels must be returned to the custodian. The custodian will retain unused portions of the sample until the State's Authorized Agent, Michael J. Hansel, authorizes that the unused samples are to be destroyed.

8. CALIBRATION PROCEDURES AND FREQUENCY

- 8.1 The procedures for internal standard or external standard calibration are described in methods 624 and 625. The laboratory is responsible for demonstrating the linear range and the linearity of the calibration curve. If the concentration level of a target compound exceeds the linear range, the extract is diluted and reanalyzed for that compound.
- 8.2 The calibration of the GC/MS system is to be verified each day by 1) achieving the DFTPP or BFB key ion abundance criteria as appropriate, 2) achieving the benzidine or pentachlorophenol tailing factor criteria as appropriate, and 3) chromatographing an aliquot of the standard solution that contains the appropriate target compounds and updating the response factors if necessary.
- 8.3 Sources of the individual target compounds are given in Table 2. The source, purity, lot number, and certificate of true values for standard solutions will be recorded.

9. ANALYTICAL PROCEDURES

- 9.1 Method 624 is to be used without change for the analysis of the purgeable samples.
- 9.2 The PNA compounds are analyzed using a procedure developed at CH₂M Hill. This procedure is very similar to method 625 with the following exceptions:
- 9.2.1 Two surrogate standards are used instead of three.
 - 9.2.2. The volume of the final extract is 0.02 mL instead of 1.00 mL.
 - 9.2.3 The internal standards are added just prior to the final concentration, subsequent analysis is performed immediately after this concentration. Method 625 calls for adding the internal standards just prior to analysis.
 - 9.2.4 The retention time agreement is to be ± 10 sec. instead of ± 30 sec.
 - 9.2.5 The MDL for the priority pollutant PNAs average less than 5 ng/L. Method 625 gives an average MDL of 3200 ng/L for the priority pollutant PNAs.

10. DATA ANALYSIS, VALIDATION AND REPORTING

- 10.1 The area of each PNA internal standard (IS) is used to judge the validity of the assay step. The area of d-8 naphthalene and d-10 anthracene must be greater than 20,000 counts and for d-12 chrysene, greater than 10,000 counts. If the area is less than that required, the GC/MS system must be retuned or the sample must be reanalyzed after additional concentration.
- 10.2 The recovery of the surrogate compounds is used to judge the validity of the sample processing steps. The surrogate standard recovery statistics are to be updated weekly to establish the control limits of $R \pm 3s$. The sample processing steps are valid if the recovery for the surrogate compounds falls within the control limits.
- 10.3 The equations in Section 7 and 15 of Method 625 are to be used to calculate the concentration of the target compounds. Report "not detected" if the calculated concentration is less than the MDL. Report the MDL concentration if the calculated concentration is between the MDL and two times the MDL. Report the concentration in $\mu\text{g/L}$ for purgeables or in ng/L for the PNAs if the calculated concentration is greater than two times the MDL.

11. INTERNAL QUALITY CONTROL CHECKS

- 11.1 Field Blanks** -- One field blank is included with each sample set. Once received back in the laboratory, the field blank is treated and an authentic sample and is used to monitor for contamination during transport and sampling.
- 11.2 Laboratory Blanks** -- A laboratory blank is analyzed whenever a field blank indicates the possibility of contamination or whenever a new lot of solvents is first used.
- 11.3 Surrogate Standards** -- All samples, including blanks, are spiked with the surrogate standards prior to extraction and are used to monitor the sample processing steps. The surrogate standards are 1-fluoronaphthalene and 2,4,6-tribromophenol.
- 11.4 Internal Standards** -- All extracts are spiked with the internal standards just prior to the final concentration. The internal standards are d-8 naphthalene, d-10 anthracene, d-12 chrysene, 2-fluorobiphenyl, and d-5 phenol.
- 11.5 Duplicates and Spiked Samples** -- The duplicate pairs are used to give overall precision of the data in both a relatively clean and a contaminated matrix. The third sample of the triplicate is used to give spiked recovery or accuracy data. The background concentration is the mean value from the two unspiked samples of the triplicate. Since the spiked samples should always be relatively clean samples, a constant amount (100 ng) of each target compound should be used in all spiked samples.
- 11.6 Refereed Samples** -- Samples sent out to the referee laboratories should include a field blank and a triplicate so that interlaboratory precision and accuracy can be compared. Capsule Labs will analyze samples using GC/MS, (modified Method 625), the Minnesota Department of Health will analyze samples using HPLC (modified Method 610), and EMSL-Cincinnati will analyze samples using HPLC method 610 and GC/MS method 625.
- 11.7 Quality Control Check Samples** -- The analytical laboratories must compare calibration standards with the EPA QC check samples at least once during this study.

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12. PERFORMANCE AND SYSTEM AUDITS

12.1 Not applicable. No formal certification program or relevant interlaboratory performance evaluation study is available or planned for these compounds at the concentrations of interest. The data from the preliminary validation study will indirectly serve as the performance and system audits.

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13. PREVENTIVE MAINTENANCE

Not applicable — The system performance checks will show whether the participants' analytical systems are operable or not; the length of time necessary to do the required research does not warrant mandatory preventive maintenance programs. However, if any maintenance is performed - during the time frame of the project - then, that maintenance must be documented.

14. SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY AND OUTLIERS

14.1 Precision -- The percent relative range (%RR) is used to assess the precision of the PAH measurements and is calculated using Equation 1.

$$\text{Equation 1} \quad \% \text{ RR} = \frac{2 * |X_1 - X_2|}{(X_1 + X_2)} * 100$$

Where: $|X_1 - X_2|$ is the absolute value of the difference between the duplicate results

The overall precision of the data set at the 95% confidence level is calculated from the average of all the %RR values using Equation 2.

$$\text{Equation 2} \quad \bar{P}_{95} = 2.51 * \frac{\sum_{i=1}^n \%RR_i}{n}$$

Where: %RR_i is each individual percent relative range
n = the number of duplicates

\bar{P}_{95} = 95% confidence level of the average precision

14.2 Accuracy -- The accuracy of the data set is determined from the analysis of the spiked samples. The accuracy for each PAH compound is calculated using Equation 3.

$$\text{Equation 3} \quad A = 100 \frac{(Z - \bar{X})}{T}$$

Where: Z - is the analytical result in ng/L for the spiked sample

\bar{X} - is the mean background concentration from the duplicate results

T - is the true value of the added spike

A - is the recovery for the added spike

The overall accuracy for each compound is the arithmetic mean over all the spiked samples, Equation 4.

$$\text{Equation 4 } \bar{A}_j = \frac{\sum_{i=1}^n A_{ij}}{n}$$

Where: A_{ij} - is each recovery value for compound j

n - is the number of spiked samples

\bar{A}_j - is the average recovery for compound j

The 95% confidence level for each mean recovery is computed using equation 5.

$$\text{Equation 5 } CL_{95} = \bar{A}_j \pm t(n-1, \alpha = 0.05) \cdot S$$

Where: $t(n-1, \alpha = 0.05)$ is the appropriate two tailed students' t at $\alpha = 0.05$

S - is the standard deviation associated with \bar{A}_j

CL_{95} - is the upper and lower 95% confidence limits of A_j

14.3 Outliers -- An outlier is an extreme value, high or low, which has questionable validity as a member of the measurement set with which it is associated. Outliers may be rejected from the data set for the following reasons.

14.3.1 A known experimental aberration occurred, such as instrument failure or there was an inconsistency in the procedure or technique.

14.3.2 The t value for the datum is larger than the tabulated two tailed students' t for $\alpha = 0.05$ at $n-1$ degrees of freedom. The t value is calculated using Equation 6.

$$\text{Equation 6 } t = \frac{(X_i - \bar{X})}{S}$$

Where: X_i - is the extreme value being tested

\bar{X} - is the mean of the measurement set for n observations

S - is the standard deviation associated with \bar{X}

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If a value is rejected, the mean (\bar{X}) and standard deviation are recalculated using the remaining data. This procedure can be reiterated using the next extreme value until no outliers remain.

15. CORRECTIVE ACTION

15.1 Corrective action is initiated whenever the system is out of control. The following criteria are used to indicate out of control situations.

15.1.1 The area of either d-8 naphthalene or d-10 anthracene internal standard is $< 20,000$ counts or the area of d-12 chrysene internal standard is $< 10,000$ counts.

15.1.2 The recovery of a surrogate standard falls outside the range of $R \pm 3s$ when R is the mean recovery and s is its associated standard deviation. This range is from 70% to 118% for 1-fluoronaphthalene at the beginning of this study and should be updated on a weekly basis.

15.1.3 The percent relative range for a given analyte of a duplicate pair exceeds 40% and the range is larger than the MDL for that analyte. This control limit is calculated using Equation 2 but substituting 3.27 for the constant 2.51 and should be updated after every fifth duplicate pair is analyzed.

15.1.4 The recovery for a spiked sample falls outside the range of $A_j \pm t(n-1, \alpha = .01) * S$ where $t(n-1, \alpha = 0.01)$ is the 99% two tailed t value for $n-1$ degrees of freedom. This range is from 48% to 118% at for all compounds the beginning of the study and should be updated for each compound after every fifth spike sample is analyzed.

15.2 If the out of control situation is due to an instrumental problem, the sample is reanalyzed after corrective action is completed. Results from the out of control analysis are discarded if the new analysis gives values that are in control.

15.3 If the out of control situation is due to other than instrumental problems, all samples analyzed between the last in control and present out of control sample are declared suspect and should be reanalyzed to ensure the validity of the data. This is just the out of control sample for the criteria in sections 15.1.1 and 15.1.2, and all samples run since the last in control duplicate for the criterion section 15.1.3, and all samples run since the last in control spike sample for the criterion in 15.1.4.

15.4 A log will be kept describing the out of control situations and the corrective action taken to remedy the situation.

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16. QUALITY ASSURANCE REPORTS TO MANAGEMENT

- 16.1 The analyst will identify and report any significant QA problems and recommend remedial steps to correct the problems.**
- 16.2 At the end of the study, a report will be made that identifies the frequency of out of control situations and the necessary corrective action, the overall precision and accuracy of the data set, and the individual outliers.**

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TABLE 1
ANTICIPATED SAMPLING SCHEDULE

Sample Set	Source	No. of Samples	Field Blanks	Duplicate	Triplicate/Spike ^a
1	Wells (12) and existing treatment (6)	18	1	1	1
2	Wells (12) and bench test (6)	18	1	1	1
3	Bench test	18	1	1	1
4	Bench test	18	1	1	1
5	Bench test	16	1	1	1
6	Bench test	16	1	1	1
7	Bench test	16	1	1	1
8	Wells (3) and pilot test (4)	7	1	1	1
9	Pilot test	4	1	-	-
10	Pilot test	4	1	1	1
11	Pilot test	4	1	-	-
12	Pilot test	4	1	1	1
13	Pilot test	4	1	-	-
14	Pilot test	4	1	1	1
15	Pilot test	4	1	-	-
16	Pilot test	4	1	1	1
17	Pilot test	4	1	-	-
TOTAL		163	17	12	12
GRAND TOTAL		204 analyses			

^a One of the triplicates is spiked at the lab to give the spiked sample.

TABLE 2
TARGET COMPOUNDS FOR GC/MS ANALYSES

<u>Compound</u>	<u>CAS</u>	<u>IONS</u>		<u>Source*</u>
		<u>Primary</u>	<u>Secondary</u>	
PNAs				
Acenaphthene	83-32-9	154	153, 152	E, N, R
Acenaphthylene	208-96-8	152	151, 153	E, N, R
Anthracene	120-12-7	178	179, 176	E, N, R
Benzo(a)anthracene	56-55-3	228	229, 226	E, N, R
Benzo(b)fluoranthene	205-99-2	252	253, 125	E, N, R
Benzo(k)fluoranthene	207-08-9	252	253, 125	E, N, R
Benzo(g,h,i)perylene	191-24-2	276	138, 277	E, N
Benzo(a)pyrene	50-32-8	252	250, 125	E, N, R
Benzo(e)pyrene	192-97-2	252	250, 125	A, S
Chrysene	218-01-9	228	226, 229	E, N, R
Dibenzo(a,h)anthracene	53-70-3	278	139, 279	E, N
Fluoranthene	206-44-0	202	101, 100	E, N, R
Fluorene	86-73-7	166	165, 167	N, R
Indeno(1,2,3-cd)pyrene	193-39-5	276	138, 277	N
1-Methylnaphthalene	90-12-0	142	141, 115	A
2-Methylnaphthalene	91-57-6	142	141, 115	A
Naphthalene	91-20-3	128	129, 127	E, N, R
Perylene	198-55-0	252	250, 126	A, S
Phenanthrene	85-01-8	178	179, 176	E, N, R
Pyrene	129-00-0	202	101, 100	E, N, R
NITROGEN HETEROCYCLES				
Acridine	260-94-6	179	178, 89	A, S
Carbazole	86-74-8	167	166, 139	A, S
Indole	120-72-9	117	90, 89	A, S
Phenanthridine	229-87-8	179	178, 151	A
Quinoline	91-22-5	129	102, 128	A

Table 2. Continued

<u>Compound</u>	<u>CAS</u>	<u>IONS</u>		<u>Source*</u>
		<u>Primary</u>	<u>Secondary</u>	
SULFUR HETEROCYCLES				
Benzo(b)thiophene	95-15-8	134	135,89	A
MISCELLANEOUS				
Biphenyl	92-52-4	154	153,76	A
2,3-Dihydroindene	496-11-7	117	118,91	A
Indene	95-13-6	116	115,89	A
AROMATIC AMINES**				

-
- * E - EPA QC Check Samples
N - NBS SRM-1647
R - EPA Repository Radian
A - Aldrich Chemical, Milwaukee, WI.
S - Sigma Chemical, St. Louis, Mo.

** Up to 3; to be chosen after first round of testing.

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TABLE 3
MDL DATA FROM VALIDATION STUDY

Compound	Spike ng/L ^a	Mean	Percent Recovery	Std. Dev.	MDL ^b	Critical F-Ratio ^c		MDL (ng/L)
						8.94	4.76	
PNAs								
Acenaphthene	25	20.4	82	1.54	4.8	15.6	1.84	1.3 ^d
	10	8.3	83	0.39	1.8			
	4	4.5	113	0.53	1.7			
Acenaphthylene	25	19.9	80	1.22	3.8	9.78	1.17	1.0 ^d
	10	7.4	74	0.39	1.8			
	4	4.3	107	0.36	1.1			
Anthracene	25	18.1	72	3.99	12.6	32.5	49.0	0.3
	10	8.0	80	0.70	3.1			
	4	3.3	83	0.10	0.3			
Benzo(a)anthracene	25	21.6	86	3.10	9.7	9.61	18.9	0.7
	10	10.9	109	1.00	4.5			
	4	4.2	104	0.23	0.7			
Benzo(b)fluor- anthene	25	22.0	88	2.81	8.8	197.	e	0.9
	10	10.9	109	0.20	0.9			
	4	e	e	e	e			
Benzo(ghi)perylene	25	19.9	80	2.66	8.4	7.84	8.81	1.0
	10	8.9	89	0.95	4.3			
	4	2.4	59	0.32	1.0			
Benzo(a)pyrene	25	17.8	71	5.48	17.2	32.6	9.0	1.0
	10	8.3	83	0.96	4.4			
	4	3.4	86	0.32	1.0			
Chrysene	25	19.6	67	3.71	11.7	55.	2.60	1.0 ^d
	10	9.5	95	0.50	2.3			
	4	3.8	95	0.31	1.0			
Dibenzo(a,h)- anthracene	25	19.7	79	2.78	8.7	5.37	7.43	1.4
	10	9.2	92	1.20	5.4			
	4	2.5	63	0.44	1.4			

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TABLE 3, Continued
MDL DATA FROM VALIDATION STUDY

Compound	Spike ng/L ^a	Mean	Percent Recovery	Std. Dev.	MDL ^b	Critical F-Ratio ^c		MDL (ng/L)
						8.94	4.76	
Fluoranthene	25	23.1	93	2.33	7.3	3.77	21.3	0.8
	10	9.4	94	1.20	5.4			
	4	4.1	102	0.26	0.8			
Fluorene	25	22.5	90	1.21	4.2	1.46	5.16	1.4
	10	7.6	76	1.00	4.5			
	4	4.4	109	0.44	1.4			
Indeno(1,2,3-cd)- pyrene	25	20.3	81	2.39	7.5	7.05	4.18	1.7 ^d
	10	8.8	88	0.90	4.1			
	4	2.6	64	0.44	1.4			
1-Methyl- naphthalene	4.5	4.5	100	0.65	2.0	-	-	2.0
2-Methyl- naphthalene	7.2	6.2	86	0.39	1.2	-	-	1.2
Naphthalene	25	20.1	80	3.71	11.7	7.02	5.63	1.9
	10	9.3	93	1.40	6.4			
	4	4.4	110	0.59	1.9			
Perylene	4	3.1	78	0.31	1.0	-	-	1.0
Phenanthrene	25	20.4	81	3.35	10.5	1.24	56.3	0.4
	10	9.8	98	3.00	13.6			
	4	4.0	101	0.13	0.4			
Pyrene	25	24.0	96	2.31	7.3	5.34	11.9	0.9
	10	11.4	114	1.00	4.5			
	4	4.4	110	0.29	0.9			

TABLE 3, Continued
MDL DATA FROM VALIDATION STUDY

ALL DATA FROM VALIDATION STUDY						Critical F-Ratio ^c		MDL (ng/L)
Compound	Spike ng/L ^a	Mean	Percent Recovery	Std. Dev.	MDL ^b	8.94	4.76	
NITROGEN HETEROCYCLES								
Acridine	4	3.6	90	0.59	1.8	-	-	1.8
Carbazole	4	3.7	93	0.34	1.1	-	-	1.1
Indole	4	5.7	143	0.93	2.9	-	-	2.9
Phenanthridine	4	4.0	99	0.46	1.4	-	-	1.4
Quinoline	5.5	6.4	116	0.22	0.7	-	-	0.7
SULFUR HETEROCYCLES								
Benzo(b)thiophene	4	3.8	95	0.21	0.7	-	-	0.7
MISCELLANEOUS								
Biphenyl	4	4.0	100	0.22	0.7	-	-	0.7
2,3-Dihydroindene	4.3	3.5	81	0.43	1.4	-	-	1.4
Indene	4.4	3.6	82	0.21	0.7	-	-	0.7
							Average	1.2

- a) Seven replicates at 25 ng/L and 4 ng/L, four replicates at 10 ng/L.
b) MDL = STD DEV* 3.143 at 25 ng/L and 4 ng/L; MDL = Std. Dev.* 4.541 at 10 ng/L
c) Pool the two most recent MDLs if F-ratio < critical value.
d) Pooled result = pooled std dev* 2.718
e) Coeluting contaminant present in this iteration.

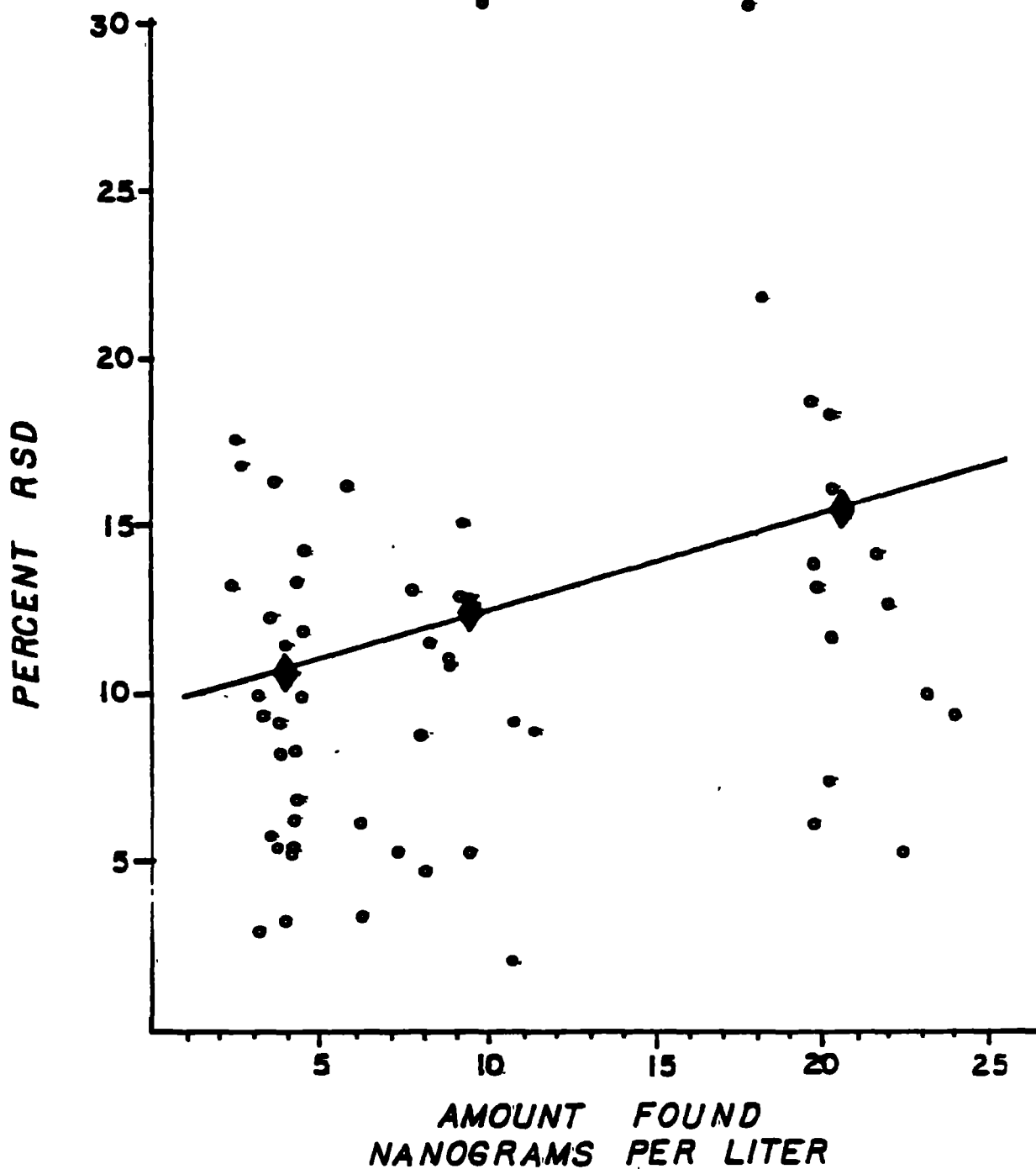


Figure 1. Relative Precision versus Concentration
in the Validation Study.

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CH₂M HILL

PH. 205/834/2870
Montgomery, Office
807 South McDonough Street
Montgomery, Alabama 36104

CLIENT _____
SAMPLE NO. _____
LOCATION _____

ANALYSIS _____

PRESERVATIVE _____
DATE _____ BY _____

Figure 2. Sample Tag for Purgeables Sample.

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[illegible]

Figure 3. Field Tracking Report Form.

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CHAIN OF CUSTODY RECORD

[illegible]

Figure 4. Chain of Custody Report Form.

SUPPLEMENT TO
"QUALITY ASSURANCE PROJECT PLAN
FOR THE MEASUREMENT OF PAH COMPOUNDS
AT ng/L LEVELS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

This document contains additional protocols and procedures to be used on the St. Louis Park investigation. The format used in this document is consistent with that used in the "Quality Assurance Project Plan for the Measurement of PAH Compounds at the ng/L Levels by Gas Chromatography/Mass Spectrometry". The additional procedures and protocols are as follows:

- 6.10 The pumps and riser pipe supplied by the contractor will be steam cleaned prior to use.
- 6.11 The sampling order for the wells without pumps will be from wells with the historical lowest levels of contamination to wells with the historical highest levels of contamination. The MPCA will provide the sampling order based on their judgement of the historical data.
- 7.6 In addition to the previously described chain of custody procedures, the following additional procedures will be used in transport of the samples:
 - 7.6.1 Prior to the time samples are to be shipped, a letter will be sent from Barr Engineering Co. to the laboratory sample custodian. The letter will contain the signatures of the authorized sample custodians from Barr Engineering Co.
 - 7.6.2 Two chain of custody documents will be used with each cooler. One will be fastened to the outside of the cooler and one will be fastened to the inside of the cooler.
 - 7.6.3 Coolers will be secured by wrapping them with several overlapping wraps of filament tape. The sample custodian will sign his or her name in waterproof ink across the wrap in the tape.

- 7.6.4 The cooler will also be secured with a special seal provided by the EPA.
- 7.6.5 The chain of custody form on the outside of the cooler will be signed by the agent accepting the cooler for the freight carrier. The chain of custody form on the outside of the cooler will also be signed by the freight carrier's agent who relinquishes custody of the cooler to the laboratory's custodian.
- 7.6.6 Prior to opening the cooler, the custodian for the laboratory will examine the seal and the tape to check for tampering.
- 7.6.7 After checking for tampering, the seal on the cooler will be broken and the signature on the chain of custody form and on the tape wraps will be compared with the previously forwarded signatures of authorized custodians. After the laboratory sample custodian is satisfied that the samples have been securely shipped, he will accept custody of the samples by signing the chain of custody form.



engineers
planners
economists
scientists

May 9, 1983

W61000.A0

Mr. Paul Bitter
USEPA 5-HR
230 South Dearborn
Chicago, Illinois 60604

Dear Paul:

I have enclosed the information you requested in our telephone conversation on May 4, 1983. This information contains a detailed description of the analytical method and a discussion of the critical factors involved in obtaining the low detection limits.

Denis Foerst has all of the QC data generated to date with the exception of the most recent pilot scale data which I am sending now.

If you should need any additional information, please let me know.

Very truly yours,

A handwritten signature in cursive script, reading "Harold E. Cole".

Harold Cole

jd/HEC/031
Enclosures

cc: Mike Harris/GLO
Denis Foerst/EPA

TRACE ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS
AND SELECTED OXYGEN, NITROGEN AND SULFUR HETEROCYCLIC
COMPOUNDS

I. SPECIAL QUALITY CONTROL MEASURES

The analysis of PAH Compounds at the low ng/l range requires special measures to prevent contamination. The following list of procedures is followed to minimize contamination problems.

o Solvents

The samples are solvent extracted with freshly distilled nanograde methylene chloride. The distillation apparatus is equipped with a distillation column packed with 90 cm of glass helices.

o Glassware

- a) Segregation - All glassware used for the trace analyses will be labeled for identification and separated from the glassware normally used for routine ppb level analyses.
- b) Cleaning - All glassware used for sample preparation will be treated as follows:
 - 1) hot soapy water wash
 - 2) ² through tap water rinse
 - 3) 20-minute treatment with chromic acid

- 4) tap water followed by distilled water rinse
- 5) nanograde acetone rinse
- 6) nanograde methylene chloride rinse.

o Sample Bottles

All sample bottles will be purchased new and equipped with teflon lined screw caps. The bottles are initially washed with hot soapy water and thoroughly rinsed with hot tap water. The bottles are then rinsed three times with nanograde acetone followed by three rinses with nanograde methylene chloride. The bottles are then inverted and allowed to air dry before shipment to the sampling site.

o General Laboratory Cleanliness

The sample preparation laboratory will be thoroughly cleaned before any analyses are performed.

II. SAMPLE EXTRACTION, CONCENTRATION AND GC/MS ANALYSIS

The following method description gives detailed step-by-step procedures used for the trace analyses. Procedure steps 1-15 are equivalent to EPA Method 625 with the exception that a two-liter sample is extracted for analysis. Procedure steps 16-19 deviate from Method 625 in degree of concentration of the final extract. Method 625 involves reducing the volume of the extract to one milliliter. This method reduces the volume to 0.02 milliliters.

Analytical Procedure

1. Transfer the sample to a two-liter separatory funnel and adjust the pH to 12 or greater.
2. Spike the sample with surrogates at an appropriate concentration (normally 50 ng/l).
3. Add 60 ml of freshly distilled methylene chloride to the sample bottle and shake for one minute.
4. Transfer the methylene chloride to the separatory funnel and shake for three minutes.
5. Allow the organic layer to separate from the water phase and collect the methylene chloride layer in a 400 ml beaker.
6. Repeat steps 3-5 two times combining the extracts in the 400 ml beaker.
7. Prepare a sodium sulfate drying column and pre-rinse the column, sodium sulfate and glass wool with 50 ml of methylene chloride.
8. Quantitatively transfer the combined extract to the drying column and collect the dried extract in a Kuderna-Danish (KD) concentrator. Rinse the drying column with 50 ml of methylene chloride.
9. Place a clean glass ebullator into the K-D flask and attach a three ball Snyder Column.
10. Place the K-D apparatus on the steam bath and concentrate to an apparent volume of 0.5 ml.

11. Remove the K-D unit from the steam bath and allow the solvent to drain and cool for at least 10 minutes.
12. Remove the Snyder Column and rinse the flask and its lower joint into the concentrator tube with 1-2 ml of methylene chloride. A 5 ml syringe is used for this operation.
13. Attach a two-ball micro-snyder column to the concentrator tube and reduce the volume of the methylene chloride to an apparent volume of 0.5 ml. Allow the solvent to drain and cool for 10 minutes.
14. Remove the micro-snyder column and rinse the joint into the concentrator tube with approximately 0.2 ml of methylene chloride.
15. Stopper the concentrator tube and place in refrigerator until GC/MS analysis.
16. Immediately prior to GC/MS analysis, remove the extract from the refrigerator and spike the extract with 20 nanograms (each) of the internal standards.
17. Thoroughly mix the internal standards with the extract using a solvent rinsed pasteur pipet. Transfer the extract into a 5 ml conical centrifuge tube.
18. Rinse the walls of the concentrator tube with an additional 0.2 ml of methylene chloride. Transfer the rinse to the centrifuge tube.

19. Reduce the volume of the extract to approximately 20 micro-liters with a gentle stream of nitrogen while warming the centrifuge tube with a heat gun.
20. Inject 2.0 microliters of the sample extract into the GC/MS.
21. After acquisition of the data, obtain Extracted Ion Current Profiles (EICP) of the primary ions for each of the PAH compounds. Determine the retention times and integrated areas under the peaks generated from the EICP.
22. Using the integrated areas of Extracted Ion Profiles for the PAH compounds and internal standards, calculate the concentrations of the PAH compounds using the following equation:

$$C_o = \frac{(A_p) (C_{is})}{(A_{is}) (RF) V_o}$$

C_o = Concentration of the pollutant in the original sample in ng/l.

A_p = The integrated area of the characteristic ion for the pollutant.

A_{is} = The integrated area of the characteristic ion for the nearest internal standard.

C_{is} = Ng of internal standard added.

V_o = The volume of the original sample in liters.

RF = Response factor determined from standards.

$$RF = \frac{(As) (Cis)}{(Ais) (Cs)}$$

As = Integrated area of characteristic ion for the pollutant standard.

Ais = Integrated area of characteristic ion for the nearest internal standard.

Cis = Amount (ng) of internal standard.

Cs = Amount (ng) of pollutant standard.

III. INSTRUMENTAL PARAMETERS

1. Gas Chromatograph - Finnigan Model 9610

Column: 30m x 0.25 mm SE-54 Fused
Silica Capillary Column (J&W
Scientific)

Injection:

Mode: Splitless
Sweep/Split Initiation: 1.0 minute
Sweep Flow: 5 cc/minute
Split Flow: 40 cc/Minute
Injector Pressure: 10 psi
Injection Temperature: 250°C

Column Temperature Program:

Initial Temperature (@ injection): 28°C
Initial Temperature (after injection):
80°C for 4 minutes

Ramp: 8°C/minute

Final Temperature: 310°C for 30 minutes

2. GC/MS Interface:

Interface Temperature: 270°C

Interface Configuration: The capillary column is coupled directly to the mass spectrometer ion source by routing the column through the interface oven and transfer line.

3. Mass Spectrometer - Finnigan Model 4000

Mode: Electron Impact

Ionizer Temperature: 260°C

Electron Multiplier Voltage: 1000-1100 volts

Dynode Voltage: 3000 volts

Electron Energy: 70 volts

Emission Current: 0.45 milliamps

Mass Scanning Range: 35-450 amu

Scan Time: 0.5 seconds/scan

4. Data System -

Computer: Data General Nova/4

Software: INCOS (24000 Compound NBS Library)

Magnetic Tape Storage: Finnigan/Perkin-Elmer

Printer: Printronix Model 300

CRT: Tektronix Model 4010-1

IV. ADDITIONAL METHOD NOTES AND EXPERIMENTAL OBSERVATIONS

- o The accuracy of obtaining a final volume of 20 microliters is not critical to the overall accuracy of the method since the procedure utilizes the internal standard method of calculation.
- o Dilute standards and internal standards have been carried through the last concentration step to check for the loss of the early eluting more

volatile compounds. The response factors did not change after the concentration process. It should be noted that multiple internal standards containing components of varying degrees of volatility are added prior to the last concentration step.

o The additional sensitivity of the method over EPA Method 625 can be attributed to the following five critical considerations:

1. The extract is concentrated to 20 microliters instead of one milliliter.
2. A two-liter sample is extracted using this method whereas a one-liter sample is normally extracted using Method 625.
3. The method utilizes a high resolution narrow bore (0.25 mm id) capillary column which substantially increases the sensitivity of the method.
4. The electron multiplier voltage is increased in such a manner as to increase sensitivity 8-10 fold. This generally requires an increase of approximately 150-200 volts on the electron multiplier since the detector approximately doubles in sensitivity for every 50 volt increase. Therefore, the standards are analyzed daily at 850-900 volts whereas the samples are analyzed at 1000-1100 volts. A comparison of dilute standards analyzed at the higher voltage and normal standards analyzed at the lower voltage indicates that the response factors are not dependent on electron multiplier voltage.

5. The instrument is equipped with a Pulsed Positive Ion Negative Ion Chemical Ionization (PPINICI) source. This configuration is equipped with dynodes which apply 3000 volts of accelerating potential to the ions before they reach the electron multiplier. Therefore, the electron multiplier can operate at much lower voltages to achieve the desired sensitivity without a substantial increase in background noise from the electron multiplier.

- o All samples analyzed are spiked with a surrogate (1-Fluoronaphthalene) to monitor extraction efficiencies. The analysis of approximately 200 samples has produced a mean percent recovery of 96% with a relative standard deviation of $\pm 11\%$. The surrogate is spiked at a concentration of 50 ng/l.
- o Concentration of the extract to 20 microliters produces detection limits in the range of 1-5 ng/l. The method is generally linear up to 100-150 ng/l at this degree of concentration. Samples of higher concentration are spiked with higher concentrations of internal standards and diluted appropriately.
- o Experience with the method to date indicates somewhat poor recoveries for a few selected high molecular weight compounds at low levels in water containing substantial hardness. The low recoveries are believed to be related to interaction of the polar compounds to the floc produced when hard water is rendered basic for extraction. This selective recovery loss was not observed during

the method validation studies which utilized soft water. Spiking at higher concentrations improves the recoveries of the polar compounds in hard water.

- o Bench-scale tests and spikes into chlorinated water indicate that chlorine readily reacts with a few selected PAH compounds.
- o Using freshly distilled methylene chloride for extraction is a critical step in the analytical procedure.

jh/HEC/029-

TECHNICAL MEMORANDUM

CH2M HILL

TO: Mike Harris/GLO

FROM: Harold Cole/MGM

DATE: May 10, 1983

SUBJECT: Tentative Identification and Quantitation of
Non-Target Parameters at SLP-15 Before and
After Treatment

PROJECT: L16334.BO.03

In our discussion with Paul Bitter on May 6, 1983, we decided to process additional data files from the pilot plant study for detectable non-target PAH parameters. The following data was obtained from SLP-15 influent and Calgon Column #1 effluent sampled on April 4, 1983 (day 42). The influent was processed first looking for any detectable and identifiable components. After tentative identifications were made in the influent, then a much more sensitive target search was performed on the data file for Column #1 effluent. The characteristic masses (base peaks) and retention times observed in the more concentrated influent sample were used to look for the components in the effluent sample. The following table reports the results of this investigation.

<u>Compounds, Identified¹</u>	<u>Influent Sample (ng/l)²</u>	<u>Effluent Sample (ng/l)²</u>
C ₁ -2,3-Dihydro-H-Indene		
Isomer 1	130	1.9
Isomer 2	130	1.4
Isomer 3	290	2.8
C ₁ -benzofuran		
Isomer 1	110	ND
Isomer 2	120	ND
Isomer 3	90	ND
C ₁ -1H-Indene		
Isomer 1	160	ND
Isomer 2	300	1.4

TECHNICAL MEMORANDUM to Mike Harris Cont'd
 Page 2
 May 9, 1983
 L16334.BO.03

<u>Compounds</u> <u>Identified</u> ¹	<u>Influent</u> <u>Sample (ng/l)</u> ²	<u>Effluent</u> <u>Sample (ng/l)</u> ²
C ₂ -Benzofuran		
Isomer 1	40	ND
Isomer 2	30	ND
Isomer 3	50	ND
C ₁ - Benz thiophene		
Isomer 1	90	ND
Isomer 2	70	ND
C ₂ -Naphthalene		
Isomer 1	100	ND
Isomer 2	170	1.3
Isomer 3	90	ND
Isomer 4	100	ND
Isomer 5	110	ND
C ₁ -Dibenzofuran		
Isomer 1	130	ND
Isomer 2	160	ND
C ₁ Phenanthrene/Anthracene		
Isomer 1	110	ND
Isomer 2	20	ND
Isomer 3	100	ND

¹ The compounds are tentatively identified from a computerized search of the National Bureau of Standards Mass Spectral Library.

² The compounds are quantitatively estimated by comparison of base peak ion currents to those of internal standards assuming a response factor of 1.0. This method of calculation can be assumed to yield minimum results since the mass spectra of the substituted isomers generally exhibit more fragmentation than those of the internal standards.

cc: Paul Bitter/EPA

jd/HEC/030